

Methane, oxygen, photosynthesis, rubisco and the regulation of the air through time

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Rubisco I's specificity, which today may be almost perfectly tuned to the task of cultivating the global garden, controlled the balance of carbon gases and O₂ in the Precambrian ocean and hence, by equilibration, in the air. Control of CO₂ and O₂ by rubisco I, coupled with CH₄ from methanogens, has for the past 2.9 Ga directed the global greenhouse warming, which maintains liquid oceans and sustains microbial ecology.

Both rubisco compensation controls and the danger of greenhouse runaway (e.g. glaciation) put limits on biological productivity. Rubisco may sustain the air in either of two permissible stable states: *either* an anoxic system with greenhouse warming supported by both high methane mixing ratios as well as carbon dioxide, *or* an oxygen-rich system in which CO₂ largely fulfils the role of managing greenhouse gas, and in which methane is necessarily only a trace greenhouse gas, as is N₂O. Transition from the anoxic to the oxic state risks glaciation. CO₂ build-up during a global snowball may be an essential precursor to a CO₂-dominated greenhouse with high levels of atmospheric O₂.

Photosynthetic and greenhouse-controlling competitions between marine algae, cyanobacteria, and terrestrial C3 and C4 plants may collectively set the CO₂ : O₂ ratio of the modern atmosphere (last few million years ago in a mainly glacial epoch), maximizing the productivity close to rubisco compensation and glacial limits.

Keywords: rubisco evolution; oxygenic photosynthesis; Archaeon; atmospheric composition

1. INTRODUCTION: PHYLOGENY AND EVOLUTION OF RUBISCO

Rubisco (ribulose 1,5-bisphosphate carboxylase/oxygenase) form I is today arguably the planet's most common protein, central to the biosphere as the chief link between atmospheric and organic carbon, and essential in managing the creation of atmospheric oxygen. Throughout the life's history, the several forms of rubisco, by facilitating gas uptake and emission into water and air, must have played a central role in directing the atmosphere. Owing to the importance of this role, and the depth of the consequent sequestration of carbon, the carbon isotopic impact of the various rubisco forms must have left an indelible geological record.

Rubisco is very ancient (Hanson & Tabita 2001; Ashida *et al.* 2005; Tabita *et al.* 2008). Form III of rubisco, comprising large subunits only, occurs in anoxic archaea, notably methanogens. Note that it is still too early to say whether all, or most, methanogens have rubisco III, though this is probable. Rubisco-like proteins (RLP or form IV), similar to the large subunit, which appear to participate in a metabolic pathway that is not the Calvin cycle, occur in some non-photosynthetic eubacteria, photosynthetic bacteria

and archaea. By contrast, rubisco form I occurs in oxic organisms. With eight large (50–55 kDa) and eight small (12–18 kDa) subunits, this is the form of the enzyme that is found in plants and cyanobacteria. Form II, found in some photosynthetic proteobacteria, chemoautotrophs and dinoflagellates, has only large subunits.

Figure 1 summarizes the possible evolution of the rubisco forms. An ancestral last common ancestor may have possessed a precursor to the rubisco family. Early on, the rubiscos diverged to an archaeal lineage that led to form III, and an anoxic bacterial lineage. All this was in anoxic conditions. At some stage, the eubacterial lineage then further diversified into form IV in strictly anoxic bacteria, and more oxygen-tolerant forms II and I in photosynthetic eubacteria. Note that in figure 1, a triple divergence is assumed, but without strong evidence.

Rubisco III in methanogens may be very old. Grassineau *et al.* (2006) found possible (though not conclusive) C isotope evidence for methanogenesis in 3.8 Ga Isua rocks. This suggests very early branching between rubisco III and eubacterial rubiscos. If so, greenhouse warming by biogenic methane may explain the puzzle of the antiquity of water-borne sediments. Methane emission is the most likely candidate for the responsibility of keeping the planetary climate warm in the earliest Archaeon, despite the faintness of the young Sun. Rubisco IV (RLP) occurs in strictly anaerobic bacteria and may have evolved in archaea (see Ashida *et al.* 2005; Tabita *et al.* 2008) in the Early or Mid-Archaeon, perhaps also the time of the original divergence between archaeal and eubacterial rubiscos.

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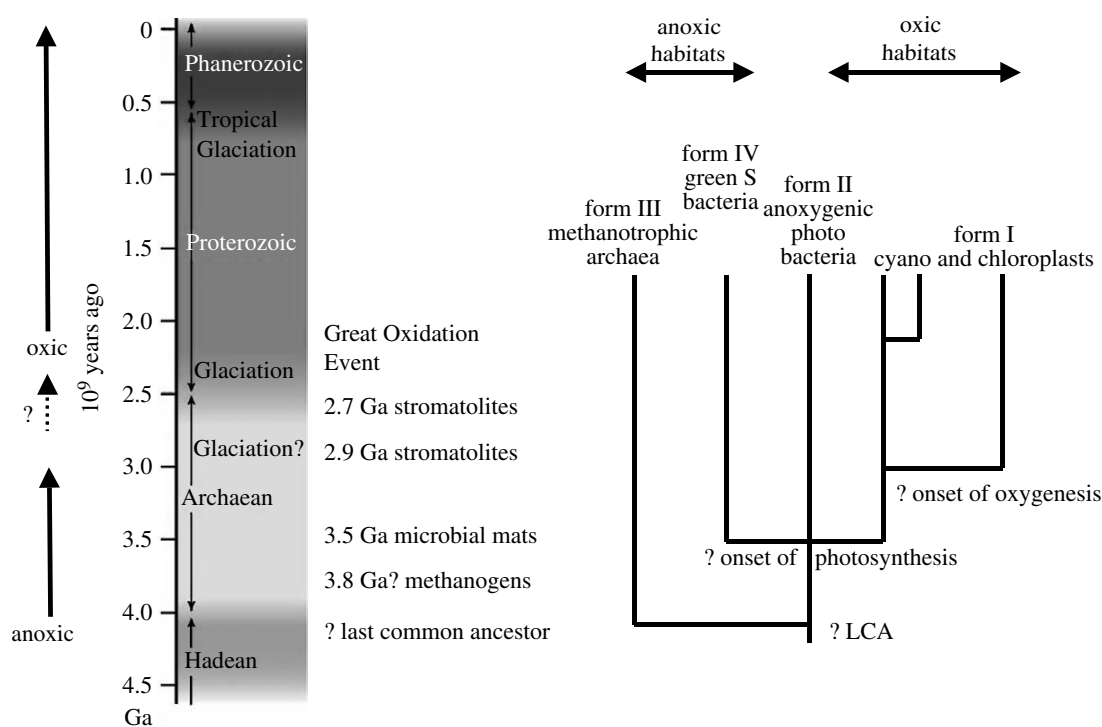


Figure 1. Outline of rubisco phylogeny (time scale adapted from Nisbet & Sleep (2001)). LCA, last common ancestor.

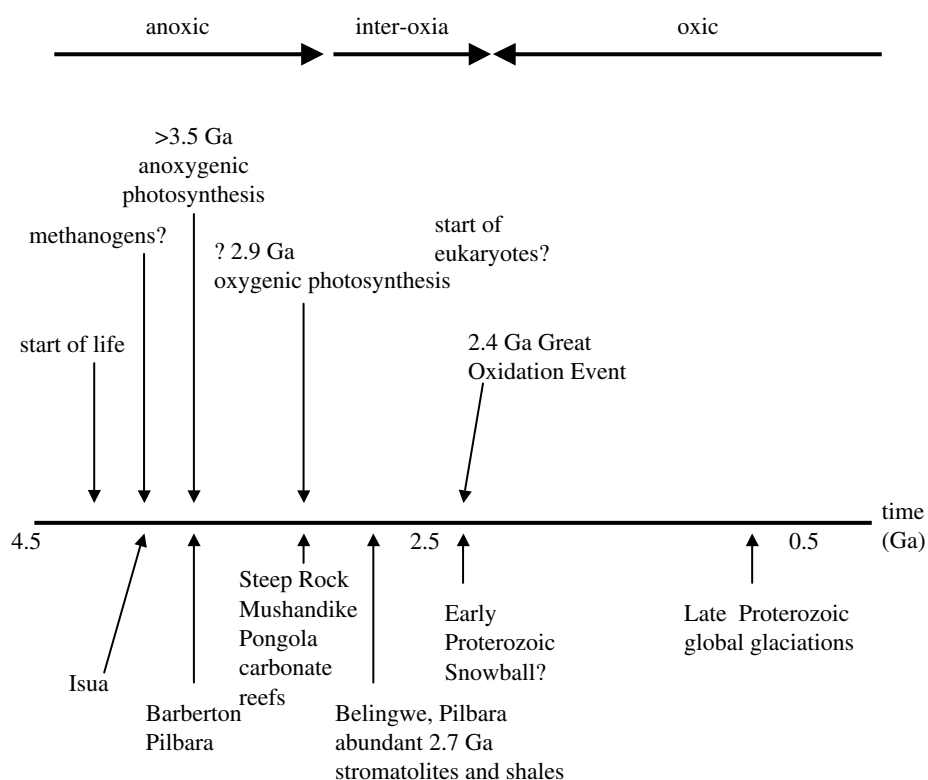


Figure 2. Outline geological record of the atmosphere (modified from Nisbet *et al.* 2007), showing timings of some key parts of the rock record.

Anoxygenic photosynthesis and rubisco II may date from the Mid-Archaean. Nisbet *et al.* (2007) studied the C and S isotopic evidence for the evolution of rubisco I and concluded that oxygenesis first had planetary impact *ca* 2.9 Ga ago. This is also the age of the oldest extant large-scale stromatolitic carbonate reefs (e.g. Wilks & Nisbet 1988). If so, this was when oxygenic

photosynthesis began on a large scale and when oxic waters first occurred (though not necessarily free oxygen in the air). Though the 2.9 Ga date may fix the appearance of rubisco I, in aerobic settings, it does not necessarily date the divergence between rubisco I and II, which must predate the oxygenesis that rubisco I made possible. Perhaps this took place in sulphate-rich waters,

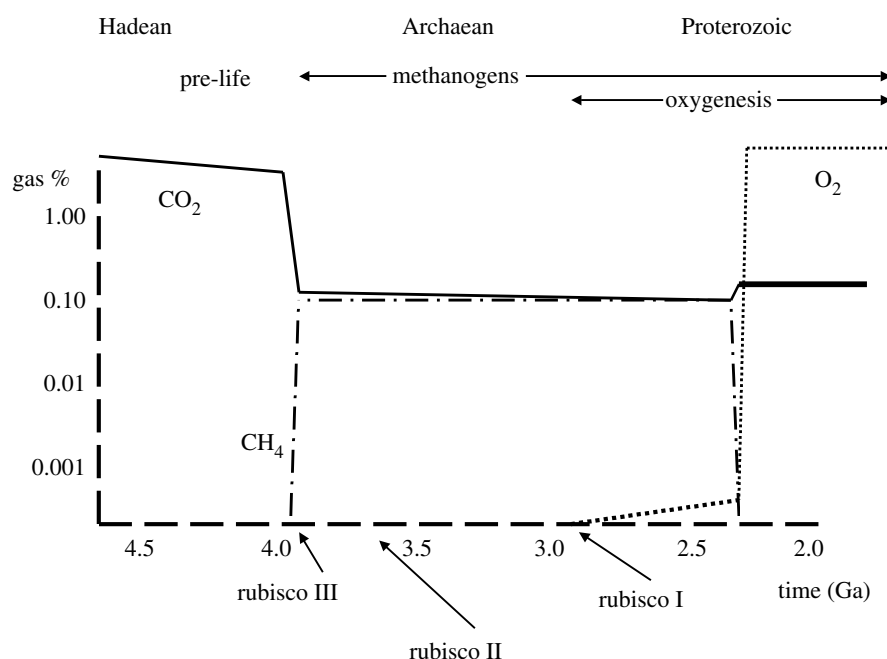


Figure 3. Possible atmospheric interpretation of geological record: hypothesis modified and updated after Lovelock (1988).

not strongly anaerobic, *ca* 3 Ga ago. Evolution of rubisco I oxygenesis would sharply increase sulphate supply and hence the productivity of the biosphere.

The evidence suggests that oxygenic photosynthesis (i.e. rubisco I) was central to microbial ecology by 2.7 Ga ago, well prior to the 2.4 Ga ‘Great Oxidation Event’ (Nisbet *et al.* 2007; Buick 2008). Abundant cyanobacterial biomarkers in shales interbedded with oxide-facies banded ironstones imply that these rocks were closely connected to the bacterial oxygen production. Brocks *et al.* (2003) reported 3 β -methylhopanes suggesting that microaerophilic heterotrophs, probably methanotrophs or methylotrophs, were active. This in turn implies the presence of archaeal methanogens 2.7 Ga ago, in agreement with the conclusions of Grassineau *et al.* (2002, 2006).

2. OXIDATION STATE AND TEMPERATURE OF THE AIR AND OCEAN IN THE ARCHAEOAN

Prior to 2.9 Ga ago, most evidence (see discussion in Nisbet *et al.* 2007) suggests that the air was anoxic (Hessler *et al.* 2004; Canfield 2005; Kasting 2006), though this consensus view has been challenged (Rosing & Frei 2004). Especially strong evidence for pre-2.9 Ga anoxia comes from non-mass-dependent fractionation of S isotopes (Farquhar & Wing 2003), which is significant, implying anoxic conditions. The S isotopic record between 2.65 and 2.9 Ga ago is more ambiguous (Farquhar *et al.* 2007). One explanation of the strongly fluctuating signal is that the air was indeed anoxic in most of the 2.65–2.9 Ga interval, but that local fluctuations in trace gas mixing ratios in photic zone waters may have occurred (Nisbet *et al.* 2007). Between 2.6 and 2.45 Ga ago, non-mass-dependent fractionation is again significant, implying anoxic conditions. Post 2.45 Ga ago, non-mass-dependent fractionation of S is absent, implying that the air has been oxidizing since the Early Proterozoic (figure 2).

The temperature of the Archaeal ocean is hotly disputed. Robert & Chaussidon (2006) argued for high

temperatures, while Sleep & Hessler (2006) suggested cooler conditions. Whatever the range, abundant sedimentological evidence implies that the oceans were in liquid state. Most preserved surface sediments are not obviously glacial. Maintenance of clement conditions under the faint Mid-Archaeal Sun would have demanded stronger greenhouse warming than today. The geological record suggests that the air had much more CO₂ *ca* 3.2 Ga ago than today (Hessler *et al.* 2004).

However, CO₂ alone might not have been capable of sustaining warm oceans, unless air pressure was markedly different. Methane is a potent greenhouse gas and Lovelock (1988), as part of a deep insight into the Archaeal puzzle that raised many hypotheses still being debated today, suggested that it may have been the chief sustainer of greenhouse warming in the time from 3.5 to 2.3 Ga ago. Under the faint young Sun, only an atmosphere with high levels of CO₂ and CH₄ would be capable of sustaining a clement, or even warm, surface. Early evolution of methanogens may have kept the planet from freezing under the faint young Sun. Figure 3 shows a possible updated version of Lovelock’s (1988) hypothesis. Kharecha *et al.* (2005) suggested that methane mixing ratios were very much higher than today (between 100 and 35 000 ppm, or 3.5%). N₂O is another possible contributor to the Archaeal greenhouse, though rarely discussed.

3. ATMOSPHERIC CONTROL: CO₂ : O₂ RATIO AND METHANE

The actions of life sustain the modern air in internal disequilibrium (O₂ and CH₄ coexisting in the same air mass) and also in disequilibrium with the geochemical setting. Dioxygen is the obverse of the carbon dioxide coin. For each O₂ molecule liberated, a molecule of CO₂ is fixed, and the reverse. At the heart of the atmospheric system are CO₂ and CH₄. These, with N₂O, are the ‘managing’ greenhouse gases, with water vapour being the chief responding gas. Climate (and the stability of oceans) is set by these gases.

CO₂ and water are taken up and O₂ is released by reactions linked to rubisco I. Though methane is generated by methanogens, today the atmospheric mixing ratio of CH₄ is also directly connected to oxygenesis and photosynthetic carbon fixation. Atmospheric CH₄ is destroyed by OH and methanotrophs, both supported by O₂. Any atmosphere that has significant O₂ thus can only contain trace amounts of CH₄. In water, oxygenesis increases sulphate supply. Methane in sediment and water is subject to anaerobic methane oxidation by sulphate-supported archaeal/bacterial consortia. Conversely, methane emission depends on photosynthetic carbon uptake, which eventually creates dead organic matter. From this, sedimentation of fixed carbon enters or creates anaerobic settings such as organic-rich sediment and eventually re-enters the ocean/atmosphere system as biologically released methane.

Several questions thus arise, given the dominance of rubisco in global biospheric carbon cycling, as follows.

- (i) Does rubisco I set the O₂ : CO₂ ratio of the atmosphere, and hence indirectly control CH₄ and O₃?
- (ii) Has the evolution of rubisco in all its forms been the factor that controlled the history of the atmospheric greenhouse?

If so,

- (iii) Has rubisco evolution, over the aeons, by its management of the greenhouse, sustained planetary habitability under a slowly brightening Sun, by controlling the radiative impact of CO₂ and CH₄, as amplified by water feedbacks?

The centre of the atmospheric puzzle is the CO₂ : CH₄ : O₂ relationship. Rubisco I, supplemented by rubisco II, controls the CO₂ : O₂ ratio, and by its oxygen emission destroys methane in oxic air, while rubisco III facilitates the creation of methane, which provides an alternative mechanism of greenhouse feedback and fosters anoxia, in which rubisco IV cells flourish.

(a) *Rubisco specificity*

Both CO₂ and O₂ can act as substrates for rubisco catalysis. Rubisco I's selection of CO₂ over O₂, or 'specificity' (i.e. its choice for C against O—Tolbert *et al.* 1995; Tcherkez *et al.* 2006), subjects the atmosphere to the limits in CO₂–O₂ space beyond which rubisco is incapable of capturing carbon from the air/ocean system (Hahn 1987).

The specificity of rubisco I determines the O₂ : CO₂ balance around a cell carrying out oxygenesis. This simple synopsis is complicated by carbon-concentrating mechanisms that aid transport. However, these are typically very efficient, so the control focuses on rubisco. Broadly, if O₂ and CO₂ are present in a living community that is entirely microbial (e.g. Early Precambrian), and other nutrients are available to a cyanobacterial cell in seawater, then the CO₂ : O₂ balance is attained when accessible CO₂ is in tens to hundreds of parts per million (ppm), and oxygen is in per cent.

The ppm CO₂ to per cent O₂ disproportion is directly set by rubisco's specificity. This cellular control on accessible CO₂ (e.g. in water close to the cell wall) in turn sets the O₂ : CO₂ ratio of the local environment (e.g. photic zone seawater). Thereby, by exchange and equilibration between air and water, rubisco specificity controls the planetary atmosphere. The evolution of land plants does not alter the rubisco control—a plant can be regarded as a spacesuit ('landsuit' would be closer) for a cyanobacterium to live on dry ground—the chloroplast in effect carries its 'ocean' with it, and thereby has more direct access to the atmosphere.

Gutteridge & Pierce (2006) and Tcherkez *et al.* (2006) pointed out that rubisco I specificity appears to be nearly perfectly optimized by evolution. Rubisco I is not inefficient, as was long thought. Natural selection has tuned the enzyme exquisitely finely to ambient CO₂ and O₂ conditions as well as to temperature, optimizing the compromise between, on the one hand, preference for CO₂ over O₂ and, on the other hand, the rate of catalytic turnover. This strategy is tuned to the ambient temperature and becomes less efficient at higher temperature.

Note that in turn, temperature depends directly on the atmospheric greenhouse. Thus, if the hypothesis that rubisco I is perfectly tuned to the temperature is accepted (Gutteridge & Pierce 2006; Tcherkez *et al.* 2006), then the hypothesis follows that rubisco I also sets global temperature to perfection. Gutteridge & Pierce (2006) compared this to Voltaire's *Candide*—rubisco has indeed found the best of all possible solutions to the task of cultivating the global garden.

(b) *Rubisco compensation: O₂ Γ and CO₂ Γ*

Rubisco molecular specificity, supported by very efficient CO₂ transport into and around the cell by carbonic anhydrase, is expressed on the macroscopic scale as 'compensation' controls (see discussion in Hahn 1987; Tolbert 1994; Tolbert *et al.* 1995). If ambient O₂ is below rubisco's O₂ compensation (known as the O₂ Γ), then there is uptake of CO₂ from the air, with the reduction of the carbon into organic matter, and plants grow. Conversely, if ambient dioxygen in the environment is above the O₂ Γ there is net photorespiratory uptake of O₂ from the environment and reduced CO₂ fixation, and plants die. The O₂ Γ level increases linearly with the mixing ratio of ambient CO₂ in the air (Tolbert 1994; Tolbert *et al.* 1995). Similarly, there is a CO₂ Γ level, defining carbon dioxide compensation, when carbon fixation falls to zero. When CO₂ is below compensation, net uptake of carbon by photosynthetic cells ceases. The CO₂ Γ level similarly increases linearly with ambient O₂ mixing ratio in the air (figure 4). These compensation boundaries limit the conditions under which the oxygenic biosphere is viable, because the balance between photosynthesis and photorespiration limits the removal of CO₂ by oxygenic photosynthesis from the air.

Experiments by Tolbert *et al.* (1995) suggested that the minimum practical limit for CO₂, assuming ambient temperature and pressure, is a few tens of ppm CO₂. This limit rises as O₂ rises. Tolbert *et al.* studied chloroplasts in tobacco plants at 20°C. Their results define a linear CO₂ compensation trend with oxygen:

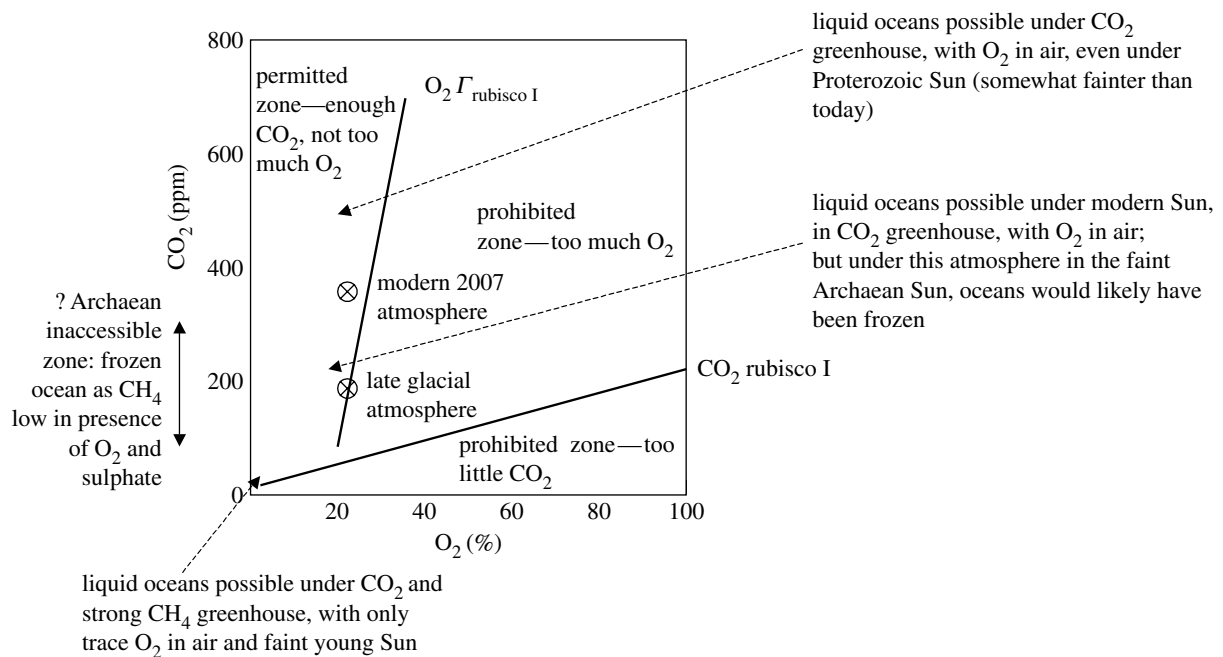


Figure 4. Rubisco compensation controls on the atmosphere. $O_2 \Gamma$ and $CO_2 \Gamma$ lines plotted from data for tobacco seedlings in Tolbert *et al.* (1995). Note the extent of permitted zone in which oxygenic photosynthesis can occur (i.e. the limits to plant, algal or cyanobacterial growth). Extension to past conditions makes the large assumption that evolutionary tuning of rubisco specificity and compensation is ancient and was similar in those past times. (Note: Assumes modern $CO_2 \Gamma$ and $O_2 \Gamma$ —i.e. early evolutionary tuning or rubisco I specificity.)

CO_2 (ppm) = $2.12 O_2$ (%) + 3.89 ppm. The maximum O_2 limit is orders of magnitude different: per cent, not ppm. This is a steep line with O_2 (%) = $0.025 CO_2$ ppm + 18%. For net growth, atmospheric CO_2 levels must be above the CO_2 line and O_2 below the O_2 line.

If tobacco plant chloroplasts exposed to abundant ambient CO_2 in the air are a representative model for the global population of oxygenic photosynthesizers, then CO_2 uptake will occur until CO_2 is drawn down to approximately 4 ppm. However, this is in optimum conditions in seedling plant cells that take CO_2 directly from the air. At sea (e.g. in the Precambrian), CO_2 is drawn from photic zone water that must access CO_2 by equilibration via carbon concentrating mechanisms with the surrounding water and thence the overlying air. In sunlight, CO_2 is rapidly depleted in local photic waters hosting a cyanobacterial bloom. For such picoplankton, the limiting local external CO_2 abundance in the air above the sea surface is therefore much higher.

Nevertheless, though seedlings have much easier access to CO_2 than microbial plankton, the Tolbert *et al.* (1995) model may have general applicability. Evolution has exquisitely tuned rubisco specificity (Gutteridge & Pierce 2006). Given the rapid turnover of microbial populations, this tuning is likely to be very ancient. Note, however, that this conclusion is qualitative. Hahn (1987) successfully modelled the balance between modern photosynthesis and photorespiration: as yet this model has not been applied to Archaean conditions.

4. REGULATION OF THE AIR: THE AIR COMPOSITION/GREENHOUSE TEMPERATURE PERMUTATION

Tolbert *et al.* (1995) showed that the late glacial (prehuman) atmosphere of 190 ppm CO_2 and 21%

O_2 was very close to the average effective compensation limits of rubisco I from plants and algae. The implication is that it is not only the atmospheric CO_2 that is near compensation but also O_2 . Evolution has driven the air to both limits, presumably to maximize productivity in a warm wet world with strong chemical erosion of nutrients from rocks. If correct, this implies long-term control by rubisco I of the $CO_2 : O_2$ ratio of the global atmosphere. In other words, by maximizing productivity (and hence 'fitness') of competing biomes (e.g. C4 grasslands versus C3 forests) and ecosystems, evolution has constrained the air composition/greenhouse temperature permutation close to the rubisco compensation control. If any perturbation occurred (e.g. volcanism, or externally driven temperature change) that pushed the atmosphere off the control line, the subsequent change in productivity would drive the system back to the compensation line on a vector in $O_2 : CO_2$ space according to the molecular balance of the uptake of the two gases.

There is a striking disproportion between the O_2 and $CO_2 \Gamma$ levels. Compensation is attained when O_2 is in per cent, but CO_2 in tens to hundreds of ppm. The difference in abundance is three orders of magnitude.

There may also be a slow long-term control exerted on (and by) the very large and long-term N_2 reservoir that forms the bulk of air pressure. The balance between nitrifying and denitrifying bacteria manages the atmospheric nitrogen reservoir and hence air pressure. Anammox planctomycetes, depending on nitrate and ammonia (which are in part linked to atmospheric oxygen and methane), also contribute to N_2 . These bacteria may be of great antiquity (Fuerst & Nisbet 2004). Nitrogenase supports the productivity by supplying fixed nitrogen, and N_2O may have been an important supplementary greenhouse gas in the

past. The role in the Archaean greenhouse of N_2O has been little studied.

There is evidence for within-cell linkage between control of nitrogen fixation by nitrogenase and the rubisco-led carbon cycle (Joshi & Tabita 1996). Globally, lightning destroys N_2 if O_2 is present; note that lightning in turn depends on atmospheric water vapour (the chief greenhouse gas and albedo controller), while NH_3 is involved in photorespiration.

The atmospheric pressure feeds back into greenhouse management by pressure broadening of the spectral absorption by greenhouse gases (C. Goldblatt 2008, unpublished data, <http://www.researchpages.net/people/colin-goldblatt>). This feedback on radiative forcing may have been a significant control. Pressure is mainly set by nitrogen. Most atmospheric modelling assumes one bar atmospheric pressure, but this assumes a partitioning of the N reservoir between air, ocean (e.g. nitrate), crust (e.g. ammonium zeolite) and mantle that may not have been valid on the Archaean planet under sustained anoxic conditions.

(a) *Management of the atmospheric greenhouse*

Greenhouse management by rubisco is, in control engineering parlance, a 'ramp' type of control system. In the atmospheric system, the small CO_2 signal controls the water greenhouse and albedo feedbacks, but the CO_2 is itself stabilized by the large O_2 reservoir. Short-term fluctuation does not easily shift this huge O_2 reservoir. Blips in CO_2 uptake or emission have little impact on O_2 . Oxygen has a lifetime of tens of millions of years in the air compared to annual production. The sharp disproportion between per cent oxygen and ppm carbon dioxide may thus sustain rubisco's long-term control on global carbon management and on the greenhouse.

Perturbations to the system are thus damped by the size of the O_2 reservoir in comparison with any probable additions or removals. Geological injections of carbon dioxide make very little impact on oxygen (see figure 6). Even doubling the CO_2 burden of the atmosphere by a volcanic emission, and increased subsequent photosynthetic release of a balancing number of moles of oxygen, will barely shift the oxygen reservoir. The system will regress to the compensation line within a few hundred thousand years, returning to the control line only very slightly upwards in O_2 space, unless it is already at the O_2 I limit. This inertia implies that the global atmosphere will absorb millions of years of progressive natural increment or excrement of CO_2 before oxygen changes significantly, especially as there are other factors at work that store reduced carbon in the near-biosphere (e.g. organic matter in sediment or methane clathrate uptake).

Was the Quaternary biosphere near the effective CO_2 I barrier as Tolbert (1994) suspected? At 21% O_2 , the line for tobacco chloroplasts gives compensation at roughly 50 ppm CO_2 . During the lifetime of oxygen (millions of years), the climate has been mostly glacial in recent times. The late glacial atmosphere, which had roughly 190 ppm CO_2 , was close to compensation. Moreover, given that the compensation lines of figure 4 are derived from tobacco chloroplasts in near-perfect laboratory conditions, not C3 and C4

plants and algal, bacterial and archaeal planktons competing for local resources, the comparison may be close. The mixing ratio of CO_2 in the air is certainly not in the per cent range.

The disproportion between CO_2 and O_2 when rubisco is close to compensation suggests two stable states of the greenhouse in which life can flourish. One state is anoxic and has greenhouse warming by a mixture of long-lived CO_2 and methane, in which trace oxygen has a short lifetime. The other state has higher CO_2 , but as a result free oxygen is permitted, and in its presence only short-lived trace methane can occur. Note that N_2O can be a significant 'warming assistant'. Rubisco biochemistry permits these two general options. Within these biologically set bounds on CO_2 : O_2 ratio, the norms of inorganic geochemistry then operate, for example, setting pH of the oceans and, more widely, responding to tectonic controls to drive the fluctuation of climate (Lowe & Tice 2007). But the biology sets the rules within which the chemistry operates, not the reverse. Goldblatt *et al.* (2006) considered the same problem of bistability. They pointed out that when O_2 mixing ratios exceed 10^{-5} of present atmospheric level, the troposphere is shielded from ultraviolet by ozone. This shielding then causes nonlinear increase in O_2 . There is here a mechanism for a catastrophic switch to an oxic stable state, in which CO_2 levels would then be governed by the compensation controls.

5. PAST RECORDS OF CO_2 , CH_4 AND O_2

Consider now the impact on the planet of the first evolution of oxygenic photosynthesis, say 2.9 Ga ago (Nisbet *et al.* 2007). Prior to this, the anoxic ocean/atmosphere system was probably kept warm by the combined greenhouse impact of both CO_2 and CH_4 , say at 1000 ppm each (Kasting 2006; Kasting & Ono 2006), possibly also with trace N_2O or NH_3 or both, from the nitrogen cycle. These gases and N_2 would have been managed collectively by a biospheric consortium of methanogenic archaea, anammox planctomycetes and anoxygenic photosynthesizers.

Photosynthetic emission of oxygen by cyanobacteria into the anoxic 2.9 Ga atmosphere would have introduced a new source of free O_2 emission. Initially, O_2 would only be at trace levels. With O_2 so low, rubisco I compensation would be attained by drawing down CO_2 to very low levels (figure 4), though as this took place, in photic zone water, local oxygen levels in the water would begin to rise. Even given the problems of accessing atmospheric CO_2 into seawater, and given the rising oxygen oases created by the new oxygenesis, CO_2 could be drawn down to, say, a few tens of ppm. In a methane-rich anoxic atmosphere, released O_2 would be short lived. Moreover, O_2 abundance would be limited by the prior mole-equivalent CO_2 inventory. Over time, eventual conversion of most of the prior atmospheric reservoir of CO_2 (say, 1000 ppm) would release a molecular equivalent amount of O_2 in the ppm range.

It is possible that, with a sudden bloom of newly evolved oxygenic cyanobacteria, rapid conversion of most of the CO_2 inventory of the air, down to

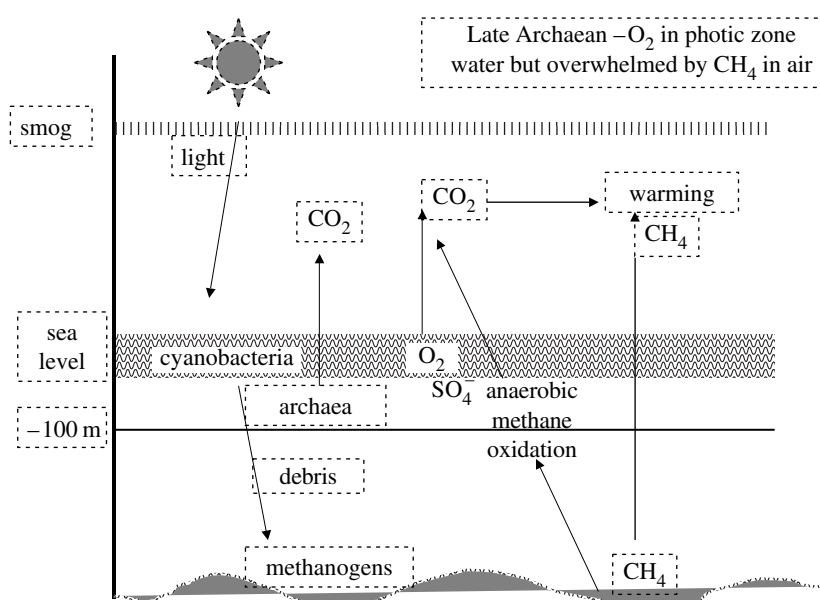


Figure 5. Synopsis of possible Late Archaean atmospheric conditions.

compensation levels at low O_2 , could trigger glaciation, especially if the methane greenhouse were reduced too. Ice cover would then limit further biological productivity. Thus, O_2 would remain in very low abundance as a minor trace gas in the air (see Farquhar *et al.* 2007).

Glaciation is not the only possible fate of a newly oxygenic biosphere. In parallel with oxygenesis, the increase in biological productivity would increase methane release by methanogens reprocessing newly abundant organic carbon. This methane could restore greenhouse warming. Though the new oxygen (and hence OH) would challenge atmospheric CH_4 , while more abundant sulphate in water would challenge methane in the sediment as it was emitted, total methane emission would be in the long-term balance oxygen output. Thus, the newly productive methanogens would support the methane mixing ratio in the air. In an anoxic prior setting with dominant CH_4 (and hence long methane lifetime, but short O_2 life), a relatively small flux of methane could sustain a significant atmospheric burden.

A possible resultant Late Archaean scenario would be the following:

- (i) a methane-rich atmosphere with abundant long-lived CH_4 , low CO_2 and short-lived trace O_2 ,
- (ii) water in which oxygenic photosynthesis was occurring, and
- (iii) methane-rich sediment, emitting CH_4 that escaped to the water and thence to the air past zones of anaerobic oxidation of methane by sulphate (figure 5).

In these anoxic-air conditions, with atmospheric oxygen only as a trace component, there would be little or no atmospheric ozone. Unless a methane smog occurred, there would be high UVB flux to the surface, as shown by the $\delta^{33}S$ record (Farquhar & Wing 2003). This would suppress the productivity of the newly evolved cyanobacteria (Tolbert 1994). The atmospheric emission of dioxygen would eventually be

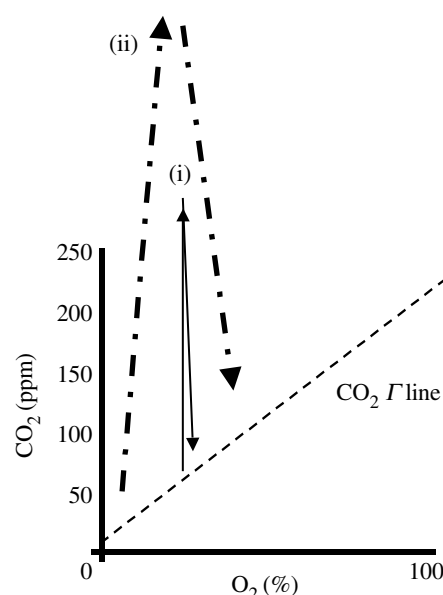


Figure 6. CO_2 emission spikes compared with recovery from Snowball Events. (i) CO_2 emission spike (e.g. from eruption of a large igneous province). Strong release of CO_2 (e.g. doubling atmospheric CO_2) causes short-term warming and flourishing photosynthesis. However, when the CO_2 has been taken up and mole-equivalent O_2 released, the impact on the much larger O_2 inventory is small. The system thus regresses close to the starting point on the compensation line (probably within a few hundred thousand years). Control by the large O_2 inventory gives stability to the system. The Palaeocene/Eocene thermal maximum may be an example. (ii) During a snowball, CO_2 from volcanic gases builds up until greenhouse warming is sufficient to initiate melting. This may occur only when CO_2 is approximately 12% (Caldeira & Kasting 1992). Once warming begins, photosynthesis restarts and this large CO_2 inventory allows a mole-equivalent O_2 release. The system regresses to the compensation line at very much higher O_2 and thus at higher CO_2 , allowing much warmer higher O_2 conditions to be sustained, compared with the system prior to the event.

taken up by the oxidation of the land surface and by the formation of seawater chemical species such as sulphate.

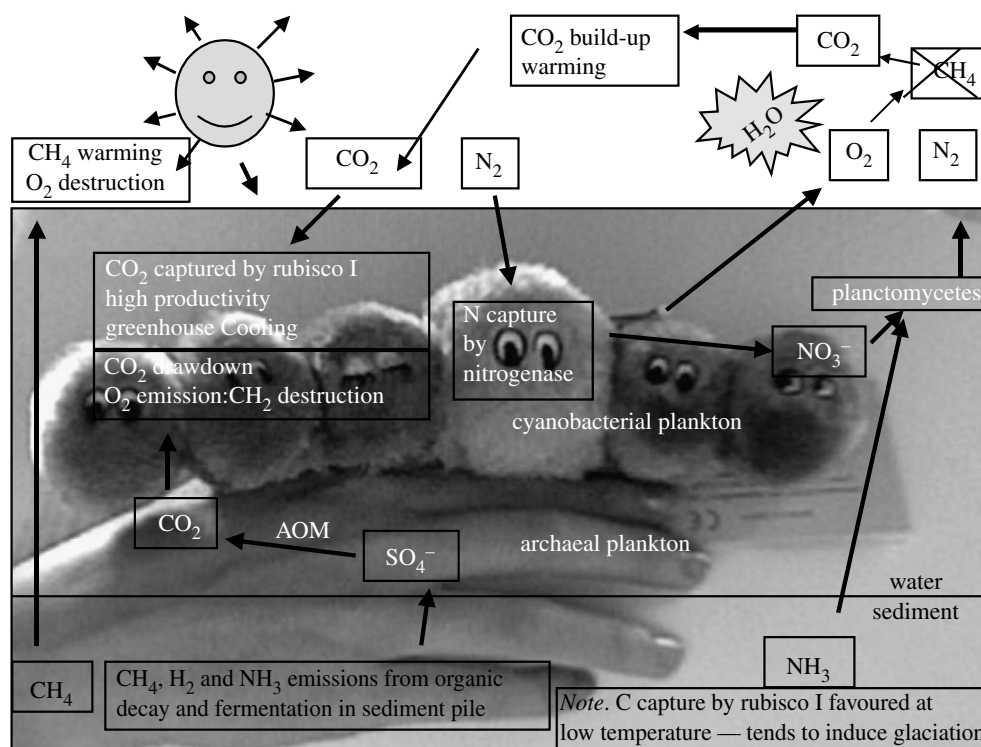


Figure 7. Cyanobacterial and other microbial controls in the Archaean ocean/atmosphere system. AOM, anaerobic oxidation of methane.

Removal of CO_2 and methane collapse as the CH_4 lifetime shortened could occur, as oxygen emission continued until sulphate abundance overcame other reductants in the exposed sediment. The collapse of atmospheric methane would end the non-mass-dependent signal in sulphur isotopes (Zahnle *et al.* 2006). This would have posed a sharp challenge to the global greenhouse, possibly initiating glaciation.

The danger of runaway cooling would be constrained. Any cooling would have been to some extent self-correcting, as it would have suppressed photosynthesis. The sediment mass is a capacitor for methane and methane hydrate. Methane emissions would continue for tens of millions of years even if the productivity of the biosphere declined or nearly ceased. Thus, though glaciation may have reduced oxygen emission, methane-driven greenhouse warming would continue, perhaps until methanotrophs and anaerobic methane oxidizers imposed equilibrium.

6. SNOWBALL EVENTS

Nevertheless, major glaciations did occur. Global glaciation may have occurred on several occasions in the Proterozoic (e.g. Hoffman *et al.* 1998). It is possible that prolonged so-called 'Snowball' Events (in the widest sense of the term) took place in the Early and Late Proterozoic. Consider the way the system would respond to the major challenge of such an event, initiated by some external process or internal dynamic. In global glaciation, photosynthesis would have been virtually shut down for tens of millions of years. If so, in these abiological conditions, the atmosphere/ocean system could have departed from the compensation line as build-up of volcanic emissions raised CO_2 , perhaps up to 12% CO_2 (Caldeira & Kasting 1992).

Greenhouse warming from such a huge inventory of volcanic CO_2 would eventually cause catastrophic breakdown of the snowball. Part of the CO_2 would then be taken up by acidophile cyanobacterial growth in the photic zone of the nutrient-rich anoxic sea. This would release equivalent moles of O_2 . Uptake of CO_2 by both organic photosynthesis and carbonate precipitation would simultaneously drive down the atmospheric CO_2 burden until, with rising O_2 and pH, and simultaneously falling CO_2 , the $\text{O}_2 : \text{CO}_2$ ratio reached the compensation barriers. This would be at the high end of the CO_2 f line, with significant free O_2 in the air (figure 6).

Recovery after a prolonged Late Proterozoic Snowball may have driven the system against the O_2 f barrier. The long-term result would be a stable oxygen-rich biosphere, with CO_2 high enough up the CO_2 f line to be the dominant managing greenhouse gas under the brighter older Sun. Possibly N_2O and other gases contributed, but once the atmospheric O_2 burden had increased, then CO_2 would dominate the forcing of water vapour, the main responding greenhouse gas, with methane's role reduced to being a short-lived trace supplementary helper. In this context, it would be interesting to introduce methane and greenhouse feedbacks into the photosynthesis/photorespiration model of Hahn (1987).

7. CONCLUDING HYPOTHESES

Consideration of the interaction of the various forms of rubisco with the atmosphere/ocean system leads to the hypothesis that rubisco has guided the evolution of the global atmosphere. By setting the $\text{O}_2 : \text{CO}_2$ ratio, and hence also the maximum abundance of CH_4 and water vapour in the air, rubisco I specificity may have controlled the greenhouse over nearly 3 Ga. In turn,

the maintenance of advantageous greenhouse conditions would confer success on cyanobacterial picoplankton, so the evolution of specificity would, conversely, be controlled by the greenhouse. The system would co-evolve.

Several further hypotheses are plausible as follows.

- (i) That rubisco compensation, the macroscopic expression of rubisco's specificity on the molecular level, is today just as finely tuned as is specificity. Together with the carbon-concentrating mechanisms, natural selection of specificity and hence of the compensation controls may maximize productivity not only of individual cells but also of consortia and biomes. This fine tuning should apply to plants, algae and cyanobacteria, according to their different settings and biochemical skills.
- (ii) That this fine tuning is very ancient, first achieved by evolutionary selection in the Archaean soon after the start of oxygenesis.
- (iii) That under anoxic air from 3.8 until 2.9 Ga ago, the greenhouse warming from methane (from rubisco III methanogens) and CO₂ (in part controlled by anoxygenic rubisco II photosynthesizers) sustained the liquid state of the oceans.
- (iv) That between 2.9 Ga ago and the Great Oxidation Event 2.4 Ga ago, both methanogens and rubisco I oxygenic photosynthesizers operated, in oxic photic zone waters under an anoxic global atmosphere with sufficient CH₄ to maintain liquid oceans, until reservoirs of reduction power (such as the deep ocean and uppermost sediments) were overwhelmed by sulphate (figure 7).
- (v) That since 2.4 Ga ago, rubisco I specificity, expressed through CO₂ and O₂ compensation, has determined the atmospheric disproportion of CO₂ (ppm) and O₂ (per cent), restricting CH₄ to trace gas status, while CO₂ alone has dominated the management of global greenhouse warming.

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